(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 1 017 016 A2

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
05.07.2000 Bulletin 2000/27

(51) Int. Cl.[7]: G06K 19/06

(21) Application number: 99204483.4

(22) Date of filing: 22.12.1999

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: 31.12.1998 US 223859

(71) Applicant: EASTMAN KODAK COMPANY
Rochester, New York 14650 (US)

(72) Inventors:
- Williams, Kevin W.,
  Patent Legal Staff
  Rochester, New York 14650-2201 (US)
- Chen, Huijuan D.,
  Patent Legal Staff
  Rochester, New York 14650-2201 (US)

(74) Representative:
Nunney, Ronald Frederick Adolphe et al
Kodak Limited,
Patents, W92-3A,
Headstone Drive
Harrow, Middlesex HA1 4TY (GB)

(54) Method for storage of data on the surface of an article

(57) This invention provides a method of storing encoded data on an article comprising applying said data on a surface of the article, as an encodement invisible to the human eye under normal viewing conditions. The invention also provides materials for use in said method.

This invention comprises an article having on a surface thereof data represented by a material applied to the article that forms a differential light pattern when illuminated which is capable of being read by a sensor capable of detecting said differential light pattern, said material being substantially invisible to the human eye under normal viewing conditions;
wherein the light absorbance of at least a portion of the surface of the article underlying said data is different from the absorbance of the material comprising the data under the conditions in which the data is read.

EP 1 017 016 A2

example fluoresce) at a different wavelength than the background reflection wavelength or the material can absorb the light and convert it to a non-irradiative energy (for example heat). Regardless of the mechanism, in conditions where the materials would be invisible these attenuations tend to be small. When applied over colored image dye these small signals are generally overwhelmed by large light absorption of the image dyes. Therefore the attenuation of the data carrying material is itself attenuated by the light characteristics of the underlying image often rendering them undetectable.

[0009] However we have discovered special conditions under which this problem can be overcome.

[0010] In accordance with one aspect of the invention, there is provided a method of storing encoded data on an article comprising applying said data on a surface of the article, as an encodement invisible to the human eye under normal viewing conditions. In preferred embodiments of the invention, the data is encoded as a two dimensional bar code.

[0011] In accordance with another aspect of the invention, there is provided the materials for storing data on an article such that these materials are invisible to the naked eye and do not interfere with the normal observation of the article under normal viewing conditions.

[0012] Yet another aspect of the invention provides for the selection of data carrying materials whose absorption and emission properties are substantially different from that of the underlying materials. Another aspect of the invention is a condition such data carrying material must have a minimal amount of absorption in visible region at a level which is detectable by a sensor at a wavelength which enables the previous aspect. Yet another aspect of the invention is when the amount of data needed to be stored requires the use of a sufficiently large area of the article where at least partially superposition of the overlying data pattern and the underlying image can't be avoided.

[0013] A further aspect of the invention comprises an article having on a surface thereof data represented by a material applied to the surface that forms a differential light pattern when illuminated with an appropriate light source which data is capable of being read by a sensor capable of detecting said differential light pattern, said material being substantially invisible to the human eye under normal viewing conditions;
wherein the light absorbance of at least a portion of the surface of the article underlying said data is different from the absorbance of the material comprising the data under the conditions in which the data is read.

[0014] Yet another aspect of this invention comprises a method of storing data which comprises applying to a surface of an article a material that forms a differential light pattern when illuminated which is capable of being read by a sensor capable of detecting said differential light pattern, said material being substantially invisible to the human eye under normal viewing conditions; wherein the light absorbance of at least a portion of the surface of the article underlying said data is different from the absorbance of the material comprising the data under the conditions in which the data is read.

[0015] In accordance with this invention a digital sensor detects the difference in light intensity of a substance relative to a background. In other words the contrast in light caused by a material. The term "differential light pattern" refers to the contrast pattern which is readable by a sensor after illumination of the material applied to the surface on an article in the form of this pattern.

[0016] In accordance with this invention it is possible to mark an article with an invisible material in a fashion where large data files can be stored on the surface of said article when the article may have existing underlying information, images or other marks.

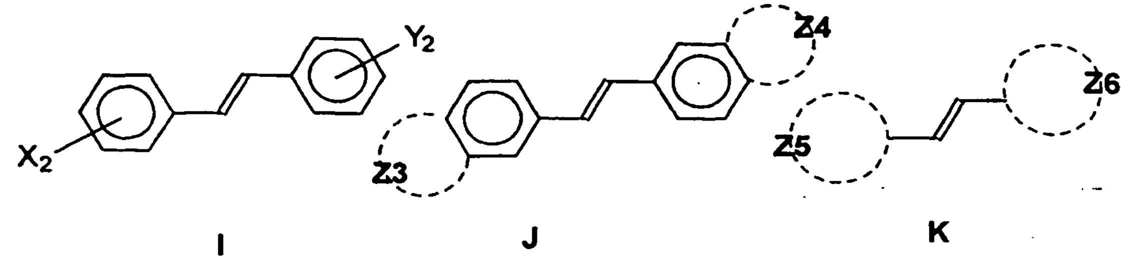
[0017] This invention is directed to those conditions which allow and enable the use of materials which when applied to a surface of an article are: 1) invisible to the naked human eye under normal viewing conditions, 2) partially or entirely over the image area of an underlying image, 3) capable of carrying large data files, 4) readable by an appropriate sensor device.

[0018] The following conditions we have found to be useful for the practice of this invention. A data carrying material should have a light absorption or emission maximum at a substantially a different wavelength maximum than that of an underlying colorant on an article. Any data carrying material is useful if the spectral overlap between such material and any underlying information, such as an image is minimized. The overall objective of any data carrying material is to provide the maximum amount of signal with the minimal amount of perceived visibility. Therefore a second requirement of the data carrying material is to have a minimal absorption visible region, i.e., from 400-700 nm.

[0019] The article can be any article on which one wants to apply encoded data. Such articles, include, for example, paper, including plain paper, glossy inkjet paper, thermal transfer receiver paper, conventional photographic paper, or transparent sheets, book cover, display windows or even on walls. The invention is particularly advantageous for encodement of invisible data on the surface of an article which contains visual information, such as a photographic or other printed image, underlying the invisible data. This enables an observer to view the underlying information at the same time as the encoded data is read by an appropriate digital reader, as discussed more fully below. In preferred embodiments of the invention the article is a still article, that is, the article does not need to be moved relative the device used to read the encoded data.

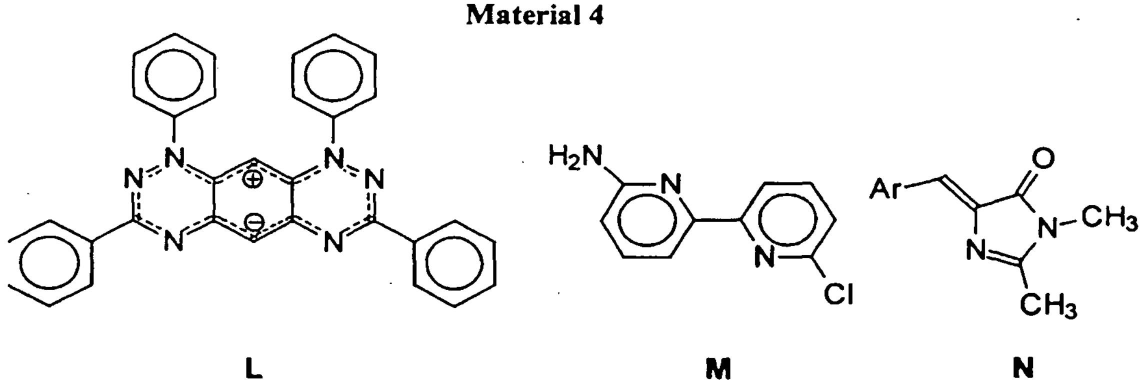
[0020] Unlike linear bar codes of the prior art, the encoded data described herein is 2-dimensional and generally

Material 3



[0030] The stilbene class of dyes (Material 3) are useful for the present invention. These dyes are very commonly used commercially as optical brightners for paper stock (see Colourage 47-52, (1995) for an excellent review of fluorescent stilbene type lumiphores). For this invention X2 and/or Y2 can be any substituent or group tat promotes absorption of this chromophore in the UV or short wavelength visible and subsequently emits light in the visible. Examples include but are not limited to halogens (for example, Cl or I,), alkyl (methyl, ethyl, butyl, or iso-amyl) which may be used to increase organic solubility, sulfonic acid and its derivatives which may be useful for increasing water solubility, carboxylic acid groups which be used for solubility but also as a position of oligomerization or polymerization. Also useful are amine derive substituents, which can be used to append groups for solubility purposes and polymerization but additionally may be used to manipulate the absorption characteristics. Stilbenes where X2 and Y2 are comprised of groups which allow for a donor and acceptor molecule in the same molecule are particularly useful for this purpose. In structures J and K, Z3, Z4, Z5 and Z6 represent any atoms that can be used to form a ring of any size or substitution with the proviso that the material is still luminescent. For structure K, it is noteworthy that Z5 and Z6 represent heteroaromatic nuclei, such as benzoxazolium,benzothiazolium,benzimdazolium,or their naphthalene derivatives, which make these compounds highly fluorescent.

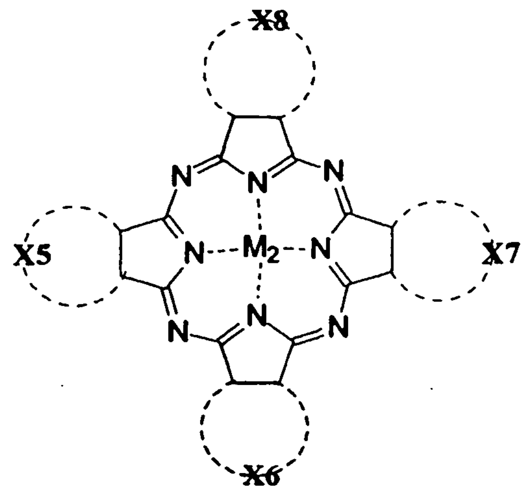
Material 4



[0031] Highly fluorescent amine heterocycles have recently been described in the academic literature and would be particularly useful for this invention. Material 4 contains several of the more recent discovered compounds described in the academic literature. The novel and highly fluorescent (ϕ~0.33) tetraphenylhexaazaanthracene (TPHA, L) is atmosphere stable and thermally stable up to 400 °C (see J. Am. Chem. Soc. *120*, 2989-2990, (*1998*)and included references). Such properties would be extremely useful for encodement of data where archival stability expects to be an important issue. The diaminobipyridine compound **M**, was found to be highly fluorescent (ϕ~0.8)and have a substantial Stokes' shift ($\Delta\lambda_{em\text{-}abs}$~100 nm), which are optical properties, that qualify these chromophores as preferred for this invention (for a literature ref. described (J. Chem. Soc., Perkin Trans. *2*, 613-617, (*1996*)). The benzimidazalones **N** are also highly fluorescent (ϕ~0.8) when incorporated into certain environments (see Tetahedron Letters, *39*, 5239-5242, (*1998*) for a recent article describing the synthesis of similar compounds). The aromatic group (Ar)can be a simple phenyl or more intricate heteroaromatic groups (imidazolo, benzoxazolo, or indole). Material 5 contains another general

the other possible colorants on articles, IR luminescent materials can be detected easier from background colorants. The next several materials are typical IR materials useful for this invention.

Material 8

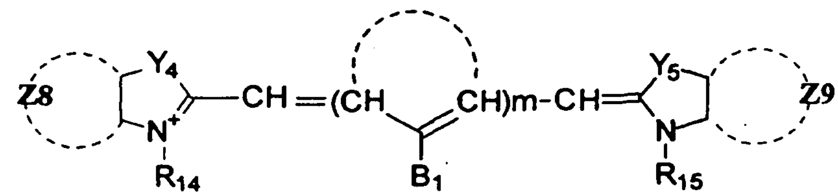


T

Material 8 contains a general structure depicting a phthalocyanine or naphthalocyanine compound. Phthalocyanines are well known in the photographic industry(for a historic reference for these compounds and their basic luminescence properties see Molecular Luminescence: An International Conference., *New York*, W. A. Benjamin, 295-307, (*1969*)). They have been used in electroconductive applications, as absorber dyes for photothermographic printing and as colorants in inks (for a general reference see chapters 5 and 9 in *Infared Absorbing dyes: Topics in Applied Chemistry.*, Edited by Masaru Matsuoka, *New York*, Plenum Press, *1990*.. Several well known properties of the phthalocyanines and their extended analogs, naphthalocyanines, have high fluorescence efficiencies (see Dyes and Pigments, *11*, 77-80, (*1989*)) for certain types and superior thermal (see Aust. J. Chem., *27*, 7-19, (*1974*))and light stability (for a recent disclosure see Dyes and Pigments, *35*, 261-267, (*1997*). These properties make these materials ideal for storage of large data amounts for extended periods as described in this invention. Compound T depicts a general structure of a phthalocyanine or naphthalocyanine. **X5, X6, X7** and **X8** represent atoms necessary to form a ring. The ring is often aromatic or heteroaromatic such as phenyl, 1,2-fused naphthyl, 1,8-fused naphthyl or larger fused polyaromatics such as fluoroanthrocyanine. The rings may be substituted in any way in the spirit of this invention provided that the materials is still luminescent. In fact differential substitution can be used to attenuate the physical properties (e.g. light stability and solubility) or enhance the optical properties of a material (e.g. Fluorescence efficiency or Stokes' shift).The rings may contain functional groups through which oligomerization can be accomplished. The **(X5-8)**-groups may be the same or different leading to symmetrical or unsymmetrical materials respectively. The metal atom **(M2)**can be any metal with the proviso that it allows for luminescent materials. The metal(**M2**) can also represent two hydrogen atoms, these materials are usually referred to as "non-metallized" (na)phthalocyanines. Some metals can possess additional "axial" ligands (e.g. Al and Si)which are useful for appending additional functional groups to alter the properties of the dyes. Additionally these groups prevent chromophore aggregation which may perturb the luminescent properties of the chromophores. These ligands also useful points of attachment for oligerimerize these materials (see Thin Solid Films, *299*,63-66, (1997)) or to create dendrimers (see Angew. Chem. Int. Ed. *37* (8), (1092-1094), (*1998*). A related class of materials is depicted in material 9. Compound **U** is classified as a "sub"-phthalocyanine (see for a lead article on the synthesis and properties of these materials J. Am. Chem. Soc. *118*, 2746-2747,(*1996*)). As for the phthalocyanines these materials are very fluorescent (ϕ~0.80). In fact these materials are useful in preparing unsymmetrical phthalocyanines. The sub-naphthalocyanines with the proper substitution can absorb in the near IR and have Stokes' shift comparable if not larger than the analogous naphthalocyanines.

actions, or encapsulation). Long chain cyanines are often bridged. It is known that such bridging

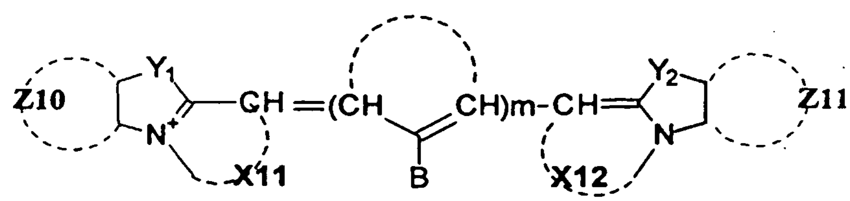
Material 11



W

has a stabilizing effect on cyanine dyes and stability is a preferred embodiment here such dyes are preferred. The bridge could be any saturated structure of any size, preferably 5, 6, 7 membered. Such ring may be functionalized with the usual groups alkyl (e.g. methyl, t-butyl) carboxlic acid (and its derivatives),sulfonic acids (and its derivatives) halogen, aromatic and heteroaromatic. Group B could be the usual chain substituents, halogen (preferable Cl), phenyl, heteroaryl (e. g. furyl, or thienyl), ethereal (e. g. ethoxy, phenoxy, or benzyloxy), or barbiturate, mercapto (e. g. thiophenoxy, or thiobenzyloxy), amino (e. g. anilino). B1 could represent a point of attachment for oligomerization or polymerization. It is noted tat m represents an integer from 1-3 as dyes containing such bridging are well known in the art. Z groups represent atoms necessary to for fused rings. Each Z group represents any ring which allows these dyes to be luminescent. Y4 and Y5 represent atoms necessary to form the typical dye nuclei and could anything which allows the material to be luminescent. Material 12 illustrates another useful feature. That is X1 and X2 represent the atoms necessary to for a ring from the nitrogen atom of the hetero-nucleus to the chromophore chain. Typically forming a 5-member or six member ring. Ridigization of chromophores as depicted in materials 11 and 12 is known to enhance the luminescence.

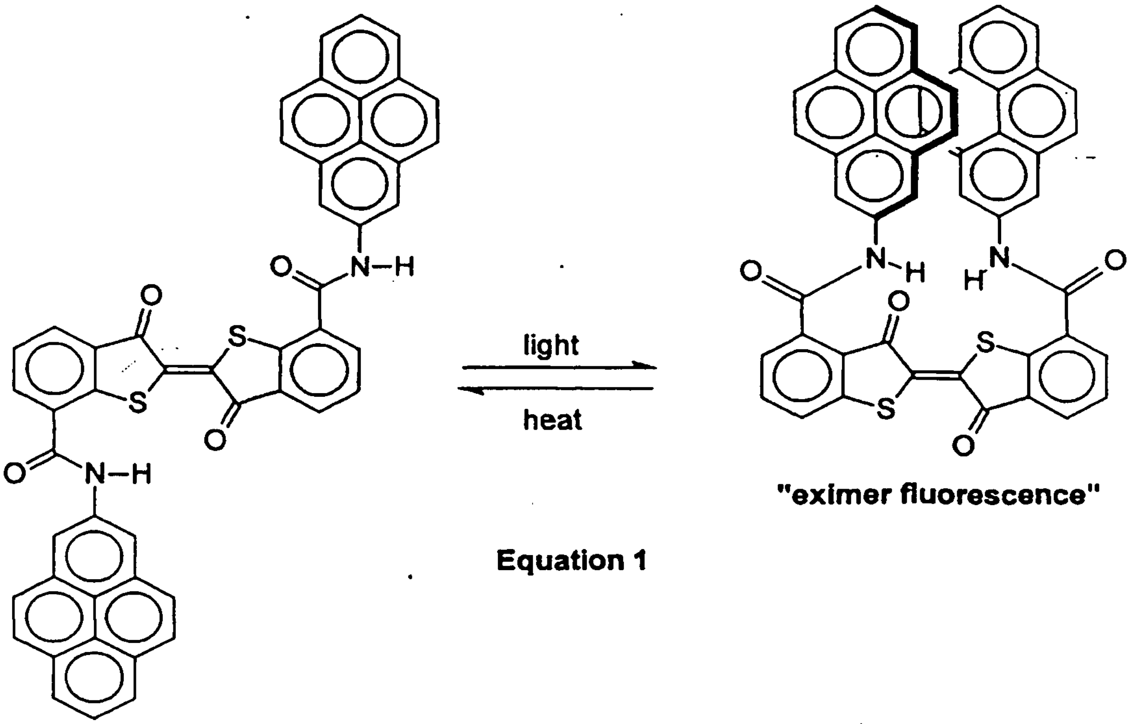
Material 12



X

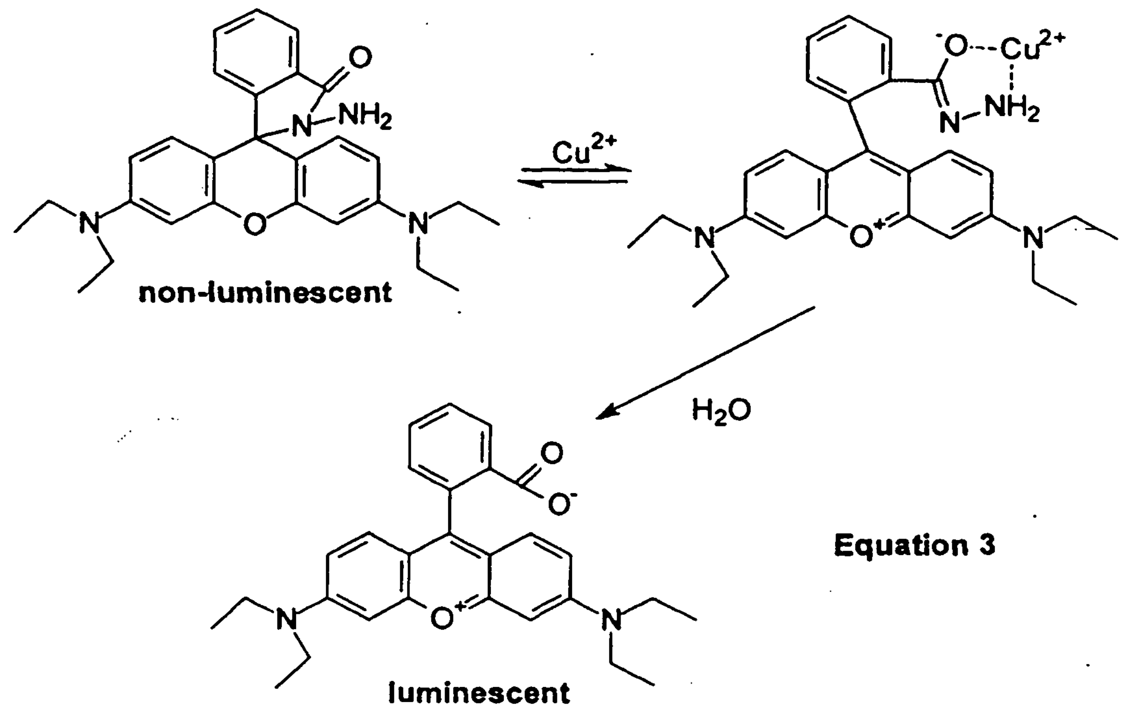
Another well known class of luminescent materials is depicted in material 13. This class of materials are known as squaraine dyes or squarylium dyes. The use of organic solubilized squaraines for antihalation protection in IR sensitive AgX applications has been described (WO 96/35142). These dyes have been also been disclosed for use as IR absorbing elements in laser addressable imaging elements (EP 0764877A1).

Material 15



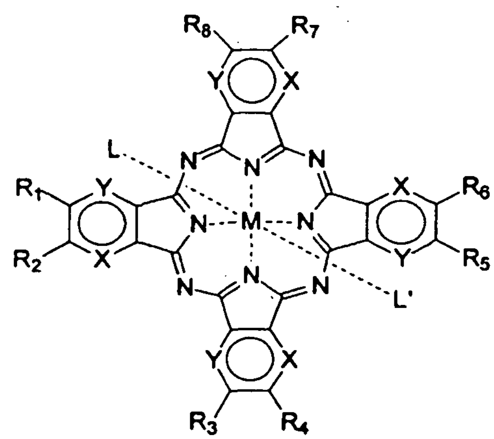
Equation 1

[0036] Equation 1 depicts the photo-conversion of a material into a material with additional "eximer fluorescence" (J. Chem.Soc.Chem. Commun., 591 (*1992*)). The process uses light to generate a new material which could be easily a luminescent material. In the above example a second point relevant to this patent is illustrated, that is, that a second stimulus (heat in the above example) may be used to reverse a material from a colored (or luminescent) state to a colorless (or non-luminescent) state. It is in the spirit of the invention that the encodement may not necessarily be due to the luminescent material directly but may be due to its removal from a luminescent background.



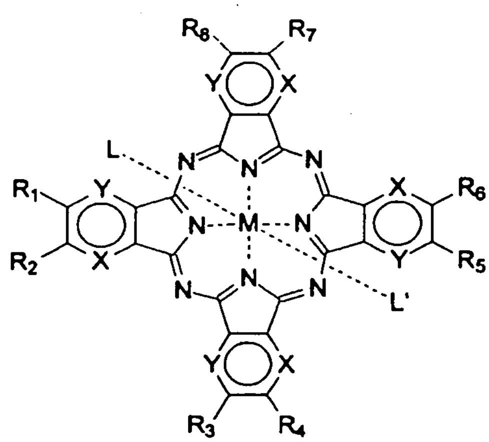
Equation 3

[0039] Specific materials that can be used in this invention include:



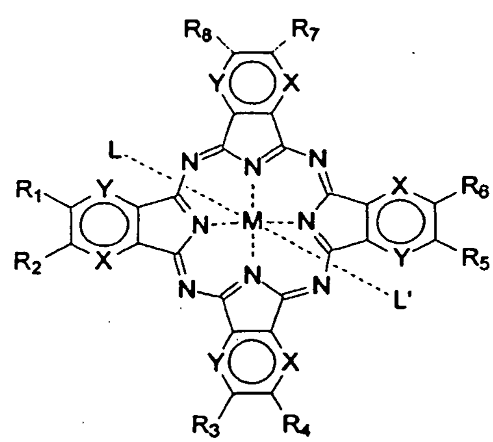
Compound	R1	R2	R3	R4	R5	R6	R7	R8	X	Y	M	L	L'
I-13	H	H	H	H	H	H	H	H	NH	CH	Al	Cl	-
I-14	H	H	H	H	H	H	H	H	NH	CH	Al	OR[a]	-
I-15	H	H	H	H	H	H	H	H	NH	CH	H2	-	-
I-16	H	H	H	H	H	H	H	H	NH	CH	Si	Cl	Cl
I-17	H	H	H	H	H	H	H	H	NH	CH	Si	OH	OH
I-18	H	H	H	H	H	H	H	H	NH	CH	Si	OR[a]	OR[a]
I-19	H	H	H	H	H	H	H	H	NH	CH	Mg	-	-
I-20	H	H	H	H	H	H	H	H	NH	CH	Zn	-	-
I-21	H	H	H	H	H	H	H	H	NH	CH	Mn	-	-
I-22	H	H	H	H	H	H	H	H	NH	CH	Sn	-	-
I-23	H	H	H	H	H	H	H	H	NH	CH	Eu	-	-
I-24	H	H	H	H	H	H	H	H	CH	CH	Yb	-	-

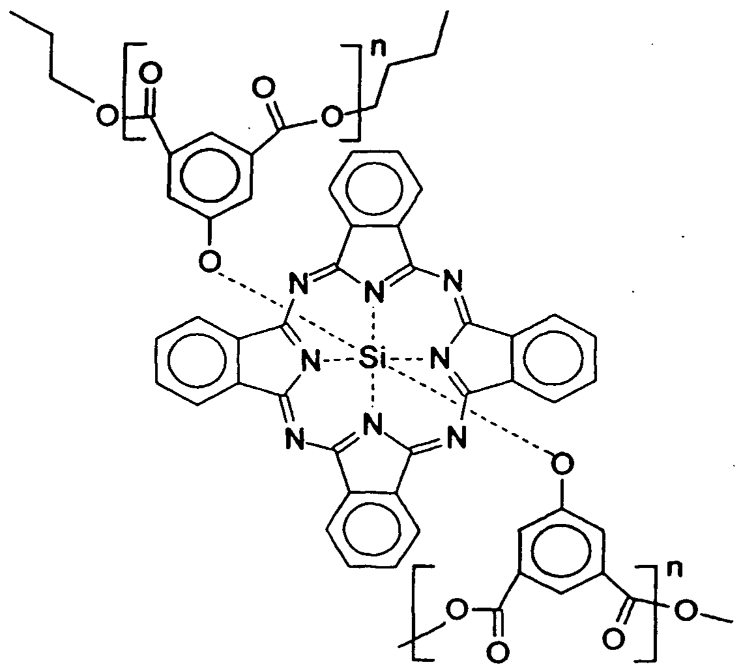
[a] R could be any substituted alkyl (methyl, ethyl, n-butyl,t-butyl, isoamyl etc...), any substituted silyl group (e.g. trimethylsilane, tributylsilane, trichlorosilane, triethoxysilane, etc...) or any gro that could be used to make the above compounds oligomeric or prevent dye aggregation)



Compound	R1	R2	R3	R4	R5	R6	R7	R8	X	Y	M	L	L'
I-37	t-butyl	H	t-butyl	H	t-butyl	H	t-butyl	H	CH	CH	Al	Cl	-
I-38	t-butyl	H	t-butyl	H	t-butyl	H	t-butyl	H	CH	CH	H2	-	-
I-39	t-butyl	H	t-butyl	H	t-butyl	H	t-butyl	H	CH	CH	Al	OR[a]	-
I-40	t-butyl	H	t-butyl	H	t-butyl	H	t-butyl	H	CH	CH	Si	Cl	Cl
I-41	t-butyl	H	t-butyl	H	t-butyl	H	t-butyl	H	CH	CH	Si	OH	OH
I-42	t-butyl	H	t-butyl	H	t-butyl	H	t-butyl	H	CH	CH	Si	OR[a]	OR[a]
I-43	t-butyl	H	t-butyl	H	t-butyl	H	t-butyl	H	CH	CH	Mg	-	-
I-44	t-butyl	H	t-butyl	H	t-butyl	H	t-butyl	H	CH	CH	Zn	-	-
I-45	t-butyl	H	t-butyl	H	t-butyl	H	t-butyl	H	CH	CH	Mn	-	-
I-46	t-butyl	H	t-butyl	H	t-butyl	H	t-butyl	H	CH	CH	Yb	-	-
I-47	t-butyl	H	t-butyl	H	t-butyl	H	t-butyl	H	CH	CH	Sn	-	-
I-48	t-butyl	H	t-butyl	H	t-butyl	H	t-butyl	H	CH	CH	Eu	-	-

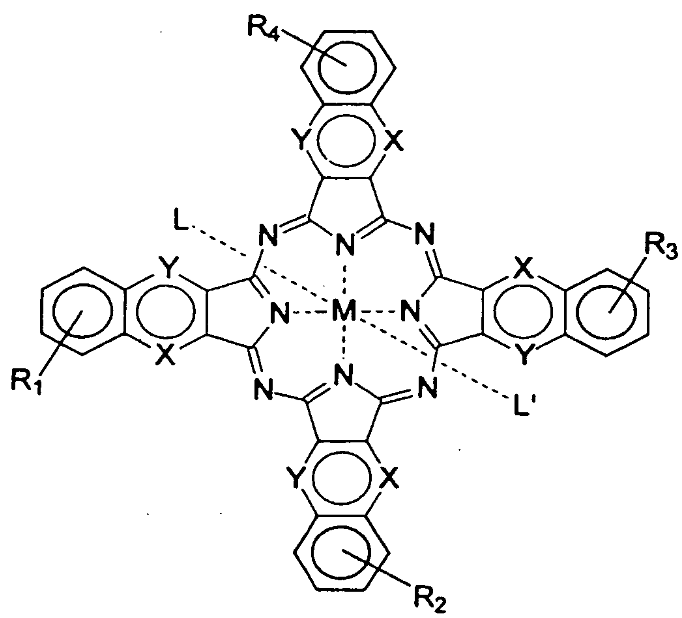
[a] R could be any substituted alkyl (methyl, ethyl, n-butyl,t-butyl, isoamyl etc...), any substituted silyl group (e.g. trimethylsilane, tributylsilane, trichlorosilane, triethoxysilane, etc...) or any gro that could be used to make the above compounds oligomeric or prevent dye aggregation)





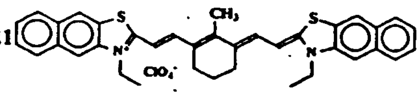
I-62

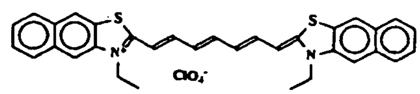
wherein n=any interger and the linkage depicts formation of any polyester

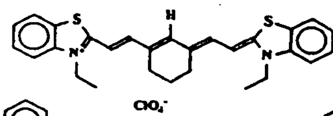


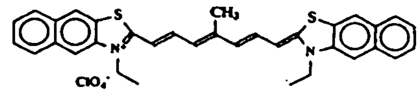
Compound	R1	R2	R3	R4	X[a]	Y[a]	M	L	L'
II-1	H	H	H	H	COR	COR	Al	Cl	-
II-2	H	H	H	H	COR	COR	H2	-	-
II-3	H	H	H	H	COR	COR	Al	OR[a]	OR[a]
II-4	H	H	H	H	COR	COR	Si	Cl	Cl
II-5	H	H	H	H	COR	COR	Si	OH	OH
II-6	H	H	H	H	COR	COR	Si	OR[a]	OR[a]
II-7	H	H	H	H	COR	COR	Mg	-	-
II-8	H	H	H	H	COR	COR	Zn	-	-
II-9	H	H	H	H	COR	COR	Mn	-	-
II-10	H	H	H	H	COR	COR	Eu	-	-
II-11	H	H	H	H	COR	COR	Sn	-	-
II-12	H	H	H	H	COR	COR	Yb	-	-

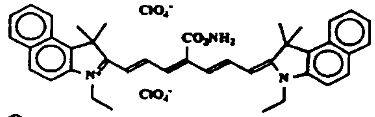
[a] R could be any substituted alkyl (methyl, ethyl, n-butyl,t-butyl, isoamyl etc. any substituted silyl group (e.g. trimethylsilane, tributylsilane, trichlorosilane triethoxysilane, etc...) or any group that could be used to make the above compounds oligomeric or prevent dye aggregation).

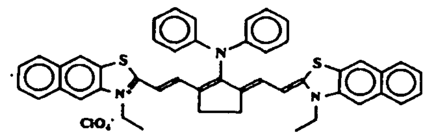
III-21 

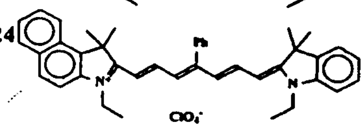
 III-29

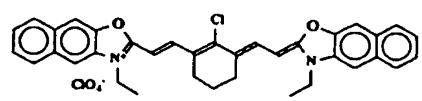
III-22 

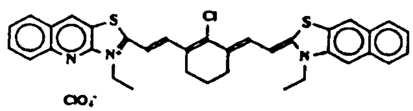
 III-30

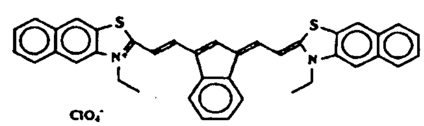
III-23 

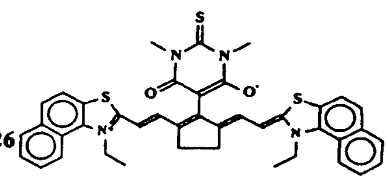
 III-31

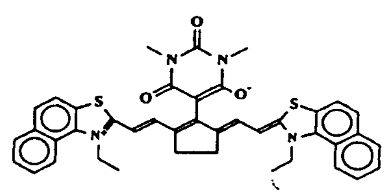
III-24 

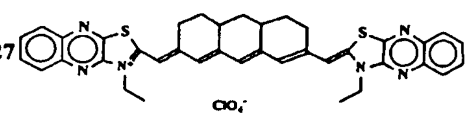
 III-32

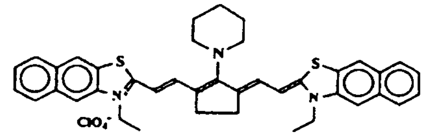
III-25 

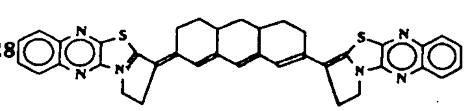
 III-33

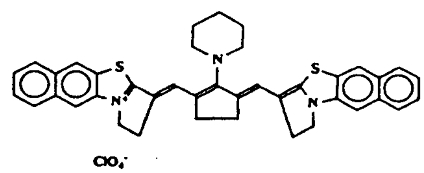
III-26 

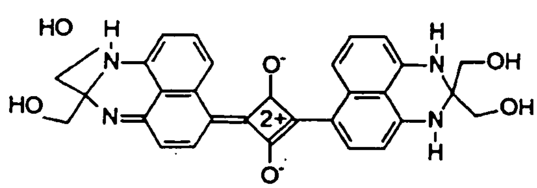
 III-34

III-27 

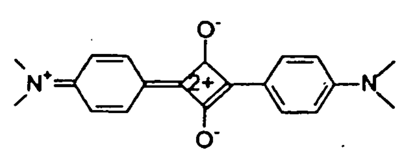
 III-35

III-28 

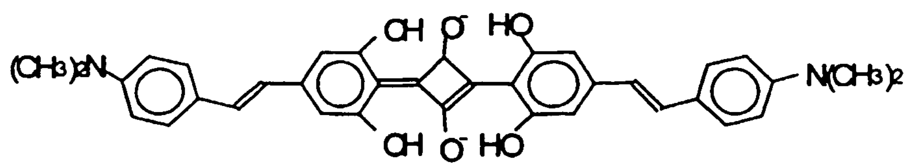
 III-36



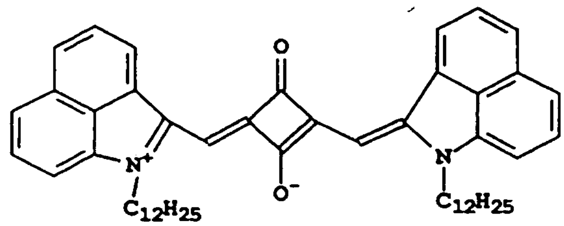
IV-1



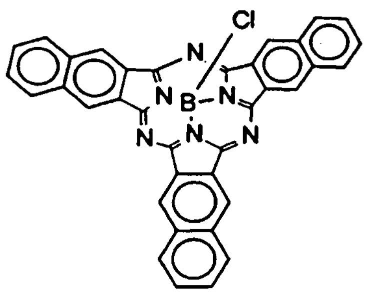
IV-2



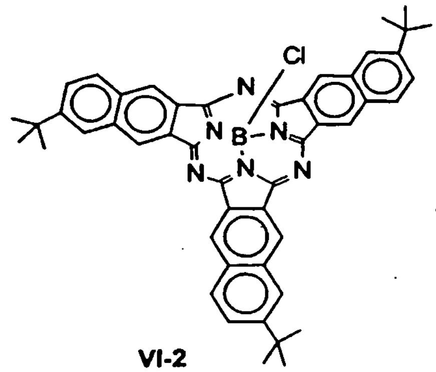
IV-13



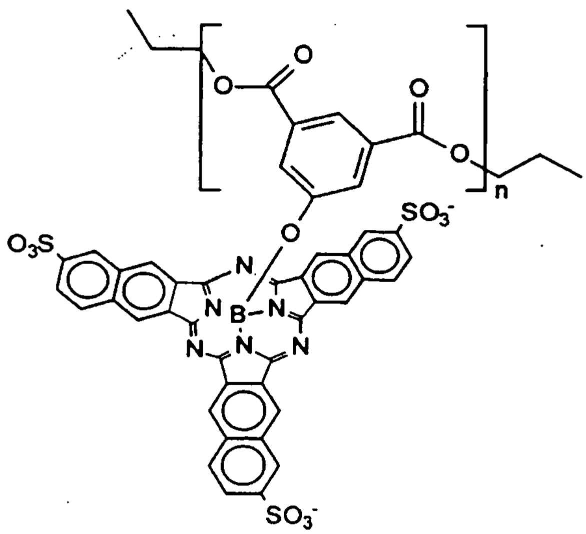
IV-14



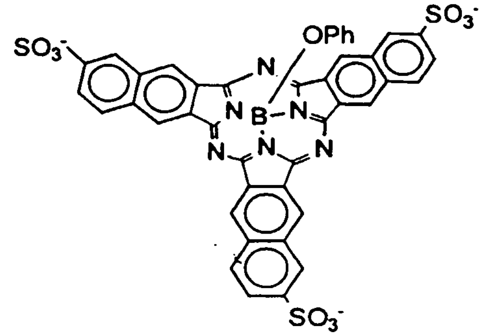
VI-1



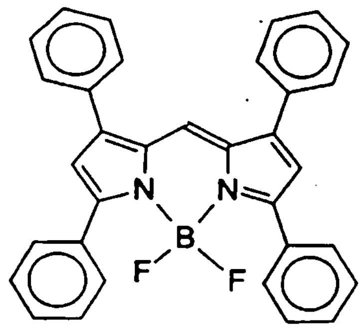
VI-2



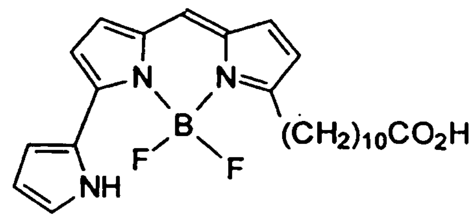
VI-3



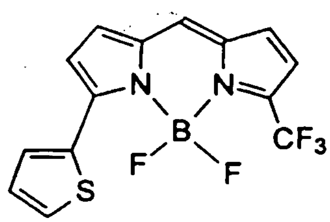
VI-4



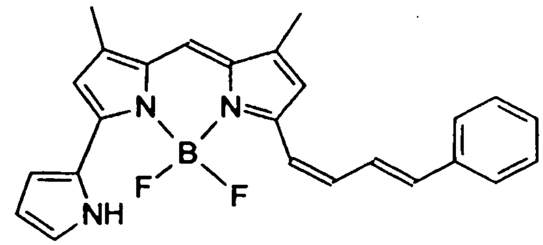
XIV-1



XIV-2



XIV-3



XIV-4

exposured with sequential red, green and blue light. The light initiates the hardening of the shell of the exposed bead rendering them resistant to destruction during the processing step. During the processing step the beads are compressed and the non-hardened beads are crushed releasing their colored dye which is the complimentary to the exposure color (red/cyan, green/magenta, blue/yellow). A discussion on methods of applying a material to a surface can be found in "Imaging Processes and Materials", chapter 1, Neblette's, 8^{th} ed., Van Nostrand Reinhold, 1989.

[0041] In the following examples inkjet and thermal dye transfer methods were chosen as the methods to apply the luminescence materials digitally on various supports.

Inkjet method

[0042] The concentration of the invisible material in the ink solution can be 0.005%~1% by weight, preferably 0.01%~0.1% by weight. A suitable surfactant such as surfynol® 465 surfactant (an ethoxylated dialcohol surfctant sold by Air Products and Chemicals, Inc.)can be added at 0.5%-2% by weight, with the presence of 2-10% glycerol, 2-10% diethyleneglycol, 2-10% propanol, and 0%-2% triethanolamine. Commercial inkjet printers such as HP690C or Epson Stylus Color 200 was used for the testing, with the printing resolution of 300 or 360 dpi. Either stepwedge files or 2-D bar-code encoding compressed sound file can be printed digitally onto various supports at the visual reflection density of 0.01-0.3, preferably 0.05-0.1.

Thermal dye transfer method

[0043] An assemblage of thermal dye transfer such as described in US 4,839,336 can be used. This assemblage comprises: (a) a dye-donor element that contains the invisible material, (b) a dye-receiving element which is in a superposed relationship with the dye-donor element so that the dye-layer of the donor element is in contact with the dye-image receiving layer of the receiving element.

[0044] The above assemblage comprising these two elements may be preassembled as an integral unit when a single luminescent dye material is transferred. This can be done by temporarily adhering the two elements together at their margins. After transfer, the dye-receiving element is then peeled apart to reveal the dye transfer image.

[0045] When a luminescent image was generated on top of a three-color thermal transferred image, dye-donor elements containing cyan, yellow and magenta dyes are used similar to that disclosed in U. S. Pat. 4,839,336. The assemblage is formed first on three occasions during the time when heat is applied by the thermal printing head. After the first dye is transferred , the elements are peeled apart. A second dye-donor element is then brought in register with the dye-receiving element and the process repeated. The third color is obtained in the same manner to generated a three-color thermal transferred image. Finally, the dye-donor element containing the luminescent material was transferred on top of the said three-color image to form a 2D (that is, a two-dimensional) bar-code file that encodes the compressed information such as sound associated with the three-color image. More than one dye donor sheet containing different luminescent materials can also be used and multiple luminescent 2D bar-code images can be transferred consecutively.

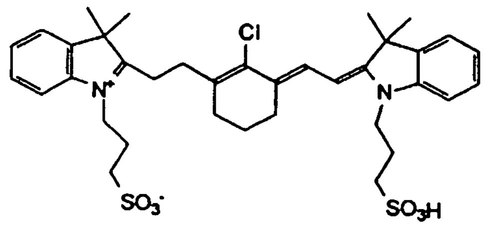
[0046] The luminescent material in the dye-donor element is dispersed in a polymer binder such as a cellulose derivatives, e. g., cellulose acetate hydrogen phthalate, cellulose acetate propionate, cellulose acetate butyrate, cellulose triacetate or any of the materials described in U. S. Pat. No. 4,700,207. The binder may be used at a coverage of from 0.1 to 5 g/m^2, and the luminescent material can be used at a coverage of from 0.02 to 0.2 g/m^2. The support for dye-donor element in this invention can be any material that is dimensionally stable and can withstand the heat of the thermal printing heads. Such materials include polyesters such as poly(ethylene terephthalate); polyamides; polycarbonates; cellulose esters such as cellulose acetate; fluorine polymers such as polyvinylidene fluoride or poly(tetrafluoroethylene-co-hexafluoropropylene); polyethers such as polyoxymethylene,; polyacetals; polyolefins such as polystyrene, polyethylene, polypropylene or methylpentane polymers; and polymides such as polymideamides and polyetherimides. The support generally has a thickness of from 2 to 30 μm. It may also be coated with a subbing layer, if desired, such as those materials described in U. S. Pat. No. 4,695,288.

[0047] The reverse side of the dye-donor element may be coated with a slipping layer to prevent the printing head from sticking to the dye-donor element. Such a slipping layer would comprise a lubricating material such as a surface active agent, a liquid lubricant, a solid lubricant or mixtures thereof, with or without a polymeric binder. Preferred lubricating materials include oils or semicrystalline organic solids tat melt below 100 °C such as poly(vinyl stearate), beeswax, perfluorinated alkyl ester polyethers, poly(caprolactone), silicone oil, poly(tetrafluoroethylene), carbowax, poly(ethylene glycols). Suitable polymeric binders for the slipping layer include poly(vinyl alcohol-cobutyral), poly(vinyl alcohol-co-acetal), poly(styrene), poly(vinyl acetate), cellulose acetate butyrate, cellulose acetate propionate, cellulose acetate or ethyl cellulose. The amount of the lubricating is generally in the range of 0.001 to 2 g/m^2. In the presence of a polymeric binder, the lubricating material is present in the range of 0.01 to 50 weight %, preferably 0.5 to 40, of the polymer binder employed.

[0048] The dye receiving element that is used with the dye-donor element of the invention usually comprise a sup-

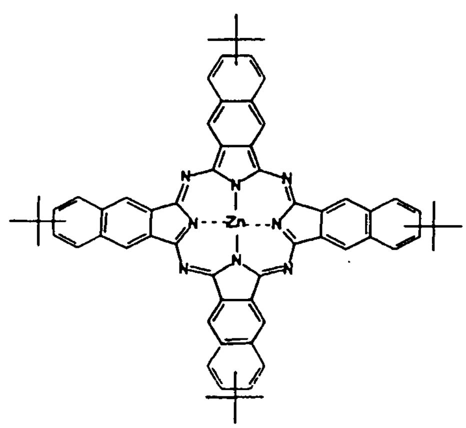
Dye 4

[0055]



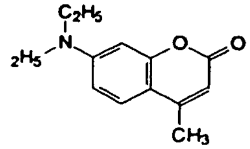
Dye 5

[0056]



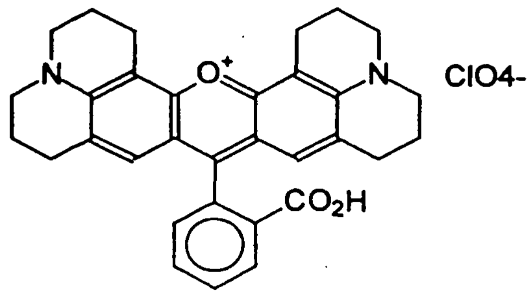
Dye 6

[0057]



Dye 10

[0061]



Example 1

[0062]

A) 1.5 g of stock solution of ink containing a near-IR dye (dye 1, 0.06% by weight,) commercially available from Eastman Chemical Company as a NIRF™ ink (PM 19599) was diluted with 13.5 g of solution containing surfynol® 465 (from Air Product), glycerol, diethyleneglycol, propanol and distilled water so that the final concentration of dye 1 is 0.006% by weight and 1% surfynol 465, 5% glycerol, 4% diethyleneglycol and 5% propanol. The resulted ink solution was filled into a refillable inkjet cartridge. A step image and a 2D bar-code image which represents a compressed sound file encoding 6 seconds of sound information were printed on glossy photographic quality inkjet papers with a HP 690C inkjet printer at 300 dpi resolution.

The step image was used to evaluate the dye spectroscopic characteristics such as reflection and fluorescence properties. The reflection spectra were obtained with the HP Lambda 19 UV/Vis/NIR spectrometer with an integrating sphere using an aperture mask to allow only the coated area of the paper be measured. The fluorescence spectra was obtained with a SPEX Fluo-2 fluorometer equipped with an IR detector at room temperature. The results are shown in Table 1.

B) An element similar to A) was prepared except that the fluorescent image was printed over inkjet printed three color image on a glossy inkjet paper instead of the blank glossy inkjet paper. The luminescent image printed was invisible to human eye under normal viewing conditions and didn't effect the quality of the color image.

C) An element similar to A) was prepared except that the fluorescent image was printed on a conventional photographic papers containing photographic images instead of the glossy inkjet paper. The luminescent image printed was invisible to human eye under normal viewing conditions and didn't effect the quality of the color image.

D). An element similar to A) was prepared except that the fluorescent image was printed on an inkjet transparency film instead of the glossy inkjet paper. The luminescent image printed was invisible to human eye under normal viewing conditions.

Example 2

Reading the 2-D luminescent bar-code:

[0063] The 2-D luminescent bar-code generated in Element 1(A) was use as an example to demonstrate the principle of detecting the luminescent 2D-barcode that encode 6 second of sound information and playing back the original sound. A 635nm red LED was used to irradiate the sample and a CCD camera was used to capture the fluorescent image. Using a commercial software (XXX), the compressed sound file was decompressed, translated and played back as a 6 second sound.

were invisible to human eye wider normal viewing conditions. The results are shown in Table 1.

B) An element similar to 6(A) was prepared except that the fluorescent image was printed over inkjet printed three color image on a glossy inkjet paper instead of the blank glossy inkjet paper. The luminescent image printed was invisible to human eye under normal viewing conditions and didn't effect the quality of the color image.

C) An element similar to 6(A) was prepared except that the fluorescent image was printed on a conventional photographic papers containing photographic images instead of the glossy inkjet paper. The luminescent image printed was invisible to human eye under normal viewing conditions and didn't effect the quality of the color image.

D) An element similar to 6(A) was prepared except that the fluorescent image was printed on an inkjet transparency film instead of the glossy inkjet paper. The luminescent image printed was invisible to human eye under normal viewing conditions.

Example 7

[0068]

A) An element similar to element 1(A) was prepared except that two fluorescent inks (one contains a near infrared-absorbing, near infrared fluorescent dye, **dye 1**, the other contains an infrared absorbing, infrared fluorescent dye, **dye 4**) and that the final concentration of **dye 1** and **dye 4** are 0.006% and 0.01% by weight, respectively, in the ink solutions. Two different luminescent 2D bar-codes (partially or completely overlap with each other) representing different compressed sound information were generated consecutively on a blank inkjet paper. The luminescent images printed were invisible to human eye under normal viewing conditions. The results are shown in Table 1.

B) An element similar to 7(A) was prepared except that the fluorescent image was printed over inkjet printed three color image on a glossy inkjet paper instead of the blank glossy inkjet paper. The luminescent image printed was invisible to human eye under normal viewing conditions and didn't effect the quality of the color image.

C) An element similar to 7(A) was prepared except that the fluorescent image was printed on a conventional photographic papers containing photographic images instead of the glossy inkjet paper. The luminescent image printed was invisible to human eye under normal viewing conditions and didn't effect the quality of the color image.

D) An element similar to 7(A) was prepared except that the fluorescent image was printed on an inkjet transparency film instead of the glossy inkjet paper. The luminescent image printed was invisible to human eye under normal viewing conditions.

Example 8

[0069]

(A) A luminescence dye-donor element was prepared by coating the following layers in the order recited on a 6 μm poly(ethylene terephthalate) support:

(1) Subbing layer of duPont Tyzor TBT® titanium tetra-n-butoxide (0.16 g/m^2) coated from a n-butyl alcohol and n-propylacetate solvent mixture, and

(2) Dye layer containing the luminescent dye (**dye 5**, a zinc naphthalocyanine derivative) shown in Table 1 (0.054 g/m^2), in a cellulose acetate propionate (2.5% acetyl, 48% propionyl) binder (0.14 g/m^2) coated from a 2-butanone and propyl acetate (80/20 ratio by weight) solvent mixture.

(3) A slip layer was coated on the back side of the element similar to that disclosed in U. S. Pat. (Henzel et a;, June 16, 1987)

A dye receiving element was similar to that disclosed in U. S. Pat. 4,839,336. A solution of Makrolon 5705®(Bayer AG Corporation) polycarbonate resin (2.9 g/m^2) in methylene chloride on a pigmented polyethlyene-overcoated paper stock to obtain the thermal receiver paper.

The dye side of the luminescent dye-donor element strip approximately 10 cm x 13 cm in area was placed in contact with the image receiver layer of the dye receiver element of the same area. The assemblage was clamped to a stepper-motor driven 60 mm diameter rubber roller and a TDK Thermal Head (No. L-231) (thermostatted at 26°C) was pressed with a force of 3.6 kg against the luminescent-donor element side of the assemblage pushing it against the rubber roller.

The imaging electronics were activated causing the donor/receiver assemblage to be drawn through the printing head/roller nip at 40.3 mm/sec. Coincidentally, resistive element in the thermal print head were pulsed for 127.75 ms/pulse at 130.75 ms intervals during a 4.575 ms/dot printing cycle (including a 0.391 ms/dot cool down

Example 12

[0073]

A) An element similar to element 1(A) was prepared except that the fluorescent dye is an infrared-absorbing, non-fluorescing dye (dye 8), and that the final concentration of dye 8 is 200 ppm by weight in the ink solution. The image printed was nearly invisible to human eye under normal viewing conditions.

B) An element similar to 12(A) was prepared except that The fluorescent image was printed over inkjet printed three color image on a glossy inkjet paper instead of the blank glossy inkjet paper. The image printed was clearly invisible to human eye under normal viewing conditions and did not effect the quality of the color image.

C) An element similar to 12(A) was prepared except that the image was printed on a conventional photographic paper containing a full color photographic image instead of the glossy inkjet paper. The image printed was clearly invisible to human eye under normal viewing conditions and did not effect the quality of the color image.

D) The invisible data file printed on the surface of the photographic article in 12(c) was read by a sensor and the sound file played back.

Table 1

Example No.	Dye No.	Absorption λ_{max} (nm)	fluorescence λ_F(nm)	Applying Method
1	1	680	686	inkjet
3	2	349	433	inkjet
4	3	430	495	InkJet
5	4	801	835	inkjet
6	2 and 4	349 801	433 835	inkjet
7	1 and 4	680 801	686 835	inkjet
8	5	775	850	thermal transfer
9	6	365	437	thermal transfer
10	7	342	613	thermal transfer
11	5 and 6	775 365	850 437	thermal transfer
12	8	890	N/A	InkJet

Notes:
1) The substrates for the luminescent bar-codes using the inkjet methods can be coated blank inkjet paper, coated inkjet paper containing inkjet printed color images, conventional photographic prints containing color images, inkjet transparencies, or any other prints.
2) The substrates for the luminescent bar-codes using the thermal transfer methods can be blank thermal transfer receiver paper or transparencies, or thermal transfer receiver paper containing thermally transferred color images.

Example 13

[0074] This example illustrates the advantageous effect of this invention. An article with conditions described in Table 2 was prepared to illustrate the effect of certain image colorants on the intensity of emitted light from a material printed on the surface above such image colorant. To practice this invention an material need be invisible and readable

3. An article of claim 2, wherein the data is sound.

4. An article of claim 1, wherein the invisible material absorbs in the UV or IR region of the spectrum.

5. An article of claim 1, wherein the invisible material is a dye

6. An article of claim 5, wherein the dye is a coumarin, a fluorescein, a rhodamine, polycyclic aromatic, , a substituted naphthalene, a naphthalene imide, a naphthalimide, a polycylic such as pyrene, a stilbene, a multi-aza fused aromatic, a bipyridyl, an imidazolone, boron complex, a transition metal complex, a lanthanide metal complex, an oxazole compound, a pyrazoline, a phthalocyanine, a naphthalocyanine, a sub-phthalocyanine, a cyanine, a squaraine, a croconium, or a metallized dye.

7. An article of claim 5, wherein the dye is oligomeric, dendreitic or polymeric.

8. An article of claim 5, wherein the invisible material is a leuco dye developed by light, by heat, by an oxidant, by a reductant, by metal complexation, or by molecular recognition.

9. An article of claim 1, wherein the invisible material is a pigment ro an inorganic salt.

10. A method of storing data which comprises applying to a surface of an article a material that forms a differential light pattern when illuminated which is capable of being read by a sensor capable of detecting said differential light pattern, said material being substantially invisible to the human eye under normal viewing conditions;
wherein the light absorbance of at least a portion of the surface of the article underlying said data is different from the absorbance of the material comprising the data under the conditions in which the data is read.

11. A method of claim 10, wherein the material is applied by printing, ink jet printing, direct thermal printing, thermal transfer, electrophotography, molecular recognition, thermal or light induced chemical reaction of a leuco dye, preferably by oxidant reaction with a leuco dye, reductant reaction with a leuco dye, or metal complexation of a leuco dye.